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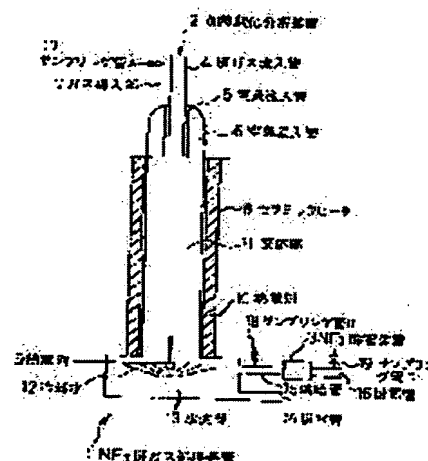
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## (54) METHOD AND DEVICE FOR TREATING WASTE NF<sub>3</sub> GAS

### (57)Abstract:

**PURPOSE:** To remove a harmful gas with high efficiency at a low running cost by heating, oxidizing and decomposing a waste NF<sub>3</sub> gas, then removing the oxidizing gas such as hydrofluoric acid and SiO<sub>2</sub> at the water washing part and removing the unoxidized NF<sub>3</sub>, etc., by the metal oxide in an NF<sub>3</sub> removal device.

**CONSTITUTION:** The waste NF<sub>3</sub> gas treating device 1 is formed with a heating, oxidizing and decomposing device 2 and an NF<sub>3</sub> removal device 3. The waste gas from its inlet pipe 4, nitrogen from its inlet pipe 5 and air from its inlet pipe 6 are introduced into the reaction part 11 of the device 2 to heat, oxidize and decompose the waste gas, and most of the NF<sub>3</sub> is oxidized and decomposed. The treated gas contg. the reaction product is washed with cooling water 12 in a washing part 13, and the waste water contg. soluble material such as F<sub>2</sub> and SiF<sub>4</sub>, SiO<sub>2</sub>, etc., is discharged outside the system. The water-washed gas is introduced into the NF<sub>3</sub> removal device 3, the unoxidized NF<sub>3</sub>, etc., are removed by metal oxides, etc., and the waste gas is purified and made harmless.



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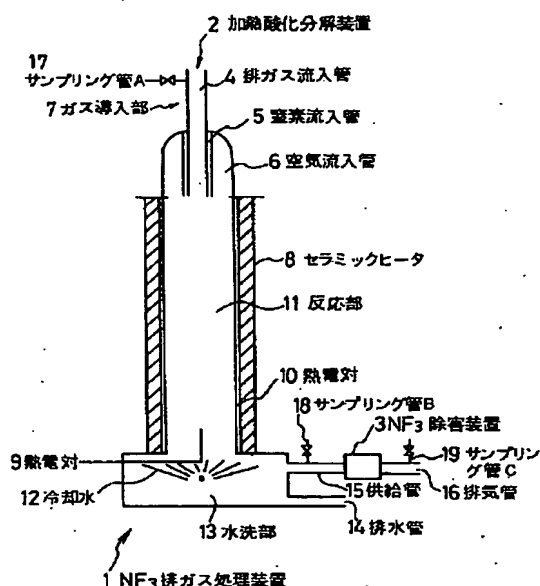
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(54) 【発明の名称】 NF<sub>3</sub> 排ガス処理方法および装置

(57) 【要約】

【目的】 本発明の目的は、ランニングコストが低廉で、かつ高い有害ガス除去率を供するNF<sub>3</sub> 排ガス処理方法およびこれを適用した装置を提供するものである。

【構成】 本発明の具体的なNF<sub>3</sub> 排ガス処理装置1は、加熱酸化分解装置2とNF<sub>3</sub> 除害装置3とから構成され、加熱酸化分解装置2の反応部11に排ガス流入管4からの排ガス、窒素流入管5からの窒素、空気流入管6からの空気とを放出して排ガスを加熱酸化分解することにより、NF<sub>3</sub>の大部分を酸化分解すると共に生成した加熱酸化分解生成物を含む処理ガスを冷却水12にて水洗部13で水洗処理し、F<sub>2</sub>、SiF<sub>4</sub>等の可溶性物質、SiO<sub>2</sub>等を含む排水を系外に排出すると共に水洗処理された処理ガスは該NF<sub>3</sub> 除害装置3に導入され、未酸化のNF<sub>3</sub>等が金属酸化物等により除害処理され、排ガスを浄化かつ無害化することができる。



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【特許請求の範囲】

【請求項1】 NF<sub>3</sub>を含む排ガスを加熱酸化分解処理し、該加熱酸化分解処理したガスに残留するNF<sub>3</sub>を除去処理することを特徴とするNF<sub>3</sub>排ガス処理方法。

【請求項2】 NF<sub>3</sub>を含む排ガスを加熱酸化分解する装置と該加熱酸化分解処理したガスに残留するNF<sub>3</sub>を除去処理する除害装置とからなることを特徴とするNF<sub>3</sub>排ガス処理装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、半導体や液晶の製造などに伴い発生するNF<sub>3</sub>排ガスを浄化して無害化する方法およびその装置に関するものである。

【0002】

【従来の技術】CVD排ガスは、未反応のプロセスガスおよびその分解で生成する有害成分を多量に含むために処理が必要である。

【0003】また、CVDのクリーニングのために用いるNF<sub>3</sub>は、クリーニング排ガスとして未反応のNF<sub>3</sub>や反応で生成するSiF<sub>4</sub>等が含有され、処理して無害化する必要がある。

【0004】従来、CVD排ガス処理には湿式スクラバーによる吸収法、固体吸着剤での吸着法、燃焼等の方法で処理されてきた。また、NF<sub>3</sub>については湿式吸収、熱分解+吸着等の処理が行われてきた。

【0005】湿式吸収の場合は、有害ガスの除去率が低い場合が多い。吸着法では除去効率は高いが吸着剤や分解剤の交換が必要でランニングコストが高い。燃焼法は可燃性ガスが対象のCVD排ガス処理には効果的であるが、クリーニングガスの処理ができない。

【0006】本発明はランニングコストが低廉で、かつ高い有害ガス除去率を供するものである。

【0007】

【課題を解決するための手段】本発明は、下記①および②記載の処理方法および装置であり、これにより上記課題を解決できる。

【0008】① NF<sub>3</sub>を含む排ガスを加熱酸化分解処理し、該加熱酸化分解処理したガスに残留するNF<sub>3</sub>を除去処理することを特徴とするNF<sub>3</sub>排ガス処理方法。

② NF<sub>3</sub>を含む排ガスを加熱酸化分解する装置と該加熱酸化分解処理したガスに残留するNF<sub>3</sub>を除去処理する除害装置とからなることを特徴とするNF<sub>3</sub>排ガス処理装置。

【0009】本発明において、NF<sub>3</sub>を含む排ガス、即ちNF<sub>3</sub>排ガス（以下、単に排ガスと言う）とは、NF<sub>3</sub>を含むガスならいかなるものでもよいが、例えば、半導体製造における少なくともNF<sub>3</sub>を含むクリーニングガスを使用する装置における排ガスを意味し、プロセスガスの排ガスに加え、装置内を該クリーニングガスにてクリーニング処理した結果生じた種々のNF<sub>3</sub>と装置内

部に存在するクリーニングすべき物質との反応生成物をも包含する意味である。従って、本発明においてNF<sub>3</sub>を除去処理するとは、NF<sub>3</sub>誘導体の除去処理をも包含する意味で使用するものとする。

【0010】本発明は、排ガスを直接に加熱酸化分解して、プロセスガス由来の排ガスにおいては、実質的に有機部分の大部をCO<sub>2</sub>と水とし、金属部分をSiO<sub>2</sub>等の金属酸化物微粒子にし、NF<sub>3</sub>においてはF<sub>2</sub>とNO<sub>x</sub>等を生じさせる。次いで、この処理ガスを所望により水洗して可溶化または巻き込みにより、微粒子、F<sub>2</sub>、SiF<sub>4</sub>等を除去してから、除害剤を充填したNF<sub>3</sub>除害装置に通すことにより、残留したNF<sub>3</sub>、NO<sub>x</sub>等を除去し、無害な処理ガスを得るものである。

【0011】本発明においては、排ガスを加熱酸化分解して、排ガスに含まれる有機部分を水とCO<sub>2</sub>に無害化し、NF<sub>3</sub>の大部、好ましくは、80%以上を酸化することにより、後段の未酸化NF<sub>3</sub>の処理量が大幅に低減されるので、NF<sub>3</sub>処理の経済性が向上するという利点を有する。

【0012】本発明において使用される除害剤とは、NF<sub>3</sub>がそのまま環境下に放出されるのを防止できる機能を有するものであれば、特に制限されず公知のものを使用できる。具体的な除害剤の例を示せば、NF<sub>3</sub>と化学的に反応してNF<sub>3</sub>の一部もしくは全部を他の化合物に変化させNF<sub>3</sub>を無害化する化学除害剤、NF<sub>3</sub>を物理的に吸着させて保持する物理除害剤、これらの併用剤等が挙げられる。

【0013】化学除害剤としては、NF<sub>3</sub>を酸化分解してF<sub>2</sub>とNO<sub>x</sub>に変化させると共にF<sub>2</sub>と化学反応するタイプが挙げられ、好ましくは鉄、マンガン、銅、珪素、チタン等の金属またはその酸化物が挙げられる。

【0014】物理除害剤としては、シリカ、活性炭、アルミナ、モレキュラーシーブ等が挙げられる。該除害剤の形態は任意であり、糸上、粉末状、他の材料、例えば、セルロース等との複合材料等が使用でき、通常、上記加熱酸化分解処理したガスの流入口とNF<sub>3</sub>を除去処理したガスの流出口を設けた容器内に所定量、充填または装填して除害装置を構成することができる。

【0015】該除害装置の温度は、化学除害剤を使用した場合300℃以上の条件で行うことが好ましい。この加熱手段はヒータ等で加熱するのがよいが、処理済排ガスとの熱交換で行うこともできる。

【0016】また、加熱酸化分解処理されたガスの除害装置における処理速度SV（流速）は2000 1/hで処理するのが望ましい。本発明における排ガスを排出する装置として、典型的にはCVD装置が挙げられ、該排ガスは、CVD処理時のプロセスガス由来のCVD排ガスおよび/またはクリーニング時のクリーニング排ガスとから構成される。

【0017】該CVD排ガスを与えるプロセスガスを例

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示すれば、無機原料としては、例えば、モノシラン、ジシラン、ジクロロシラン等、有機原料としては、例えば、TEOS（テトラエトキシシラン）、TMB（トリメトキシボラン）等があり、これらは1種以上単独または組み合わせて用いられる。これらの排ガスには、これらの未反応物あるいはその誘導体、反応分解物、例えば、 $H_2$ 、 $CO$ 、 $C_2H_5OH$ 等のアルコール、 $CH_3CHO$ 等のアルデヒド、 $C_2H_4$ 等の炭化水素等の加熱酸化分解性物質が含まれ、加熱酸化分解されることにより、主として、 $SiO_2$ 等の金属酸化物、 $H_2O$ と $CO_2$ になる。ここで言う加熱酸化分解とは、分解不能のものの単なる酸化、例えば、水素、金属等の単体の酸化等をも包含することは明らかである。

【0018】該クリーニング排ガスは、少なくともNF<sub>3</sub>とCVD装置内物質（未排気のCVD処理済物質等）との反応物、例えば、 $SiF_4$ 、NF<sub>3</sub>誘導体等、およびクリーニングガスとクリーニングガスにより物理的にクリーニングしたCVD内物質等からなる。

【0019】クリーニングガスとしては、他に $CF_4$ 、 $C_2F_6$ 、 $SF_6$ 、 $ClF_3$ などが挙げられる。本発明における加熱酸化分解処理の反応条件、排ガスの導入条件等は特に制限されるものではないが、少なくとも酸素の共存下に排ガスに含有される加熱酸化分解性物質が加熱酸化分解されればよい。従って、排ガスを加熱酸化分解装置に導入する時、同時に酸素が加熱酸化反応部に存在することが必要である。この酸素の存在方法は任意であるが、該酸素は通常排ガスと共に酸素含有ガス、例えば、空気等として導入することが好ましい。また、加熱酸化分解の条件を調整するために任意のガスを混在させることができる。例えば、窒素等の不活性ガスを混在させ、該窒素ガスが排ガスを包みかつ酸素がこれらを包むような3層状態で加熱酸化分解装置の反応部に導入されることが好ましく、加熱酸化分解装置にこれらのガス導入部として同心状に管を3層構造にしたものを配備することが好ましい。

【0020】また、加熱酸化分解処理における加熱手段も任意であるが、好ましくは、上述のように電気的に温度制御可能なヒータ加熱方式が望ましく、通常反応部の壁内に設けることができる。また、反応部の温度は、800～1000℃の範囲が好ましい。

【0021】本発明において、加熱酸化分解処理された排ガスはその組成に応じて、そのままNF<sub>3</sub>を除去する除害装置に移行させるか、更に他の任意の処理を加えてから除害装置に移行させることができる。

【0022】特に、本発明においては加熱酸化分解処理された排ガスを水と接触させること、即ち、水洗処理に供することが好ましく、これにより、該分解処理により生成した $SiO_2$ 等の金属酸化物微粒子の巻き込みによる除去、 $SiF_4$ 、F<sub>2</sub>等の水溶性化合物等の可溶性化による除去、処理ガスの冷却等を行うことができる。この

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水洗処理の方法は任意であるが、噴霧状に処理ガスと接触させることが好ましい。

【0023】この水洗処理されたガスをNF<sub>3</sub>除害処理したものは、環境に放出もしくは更に所望により他の任意の処理、例えば、公知の吸着処理等を施すことができ、任意の排気手段、例えば、排気管等を除害装置に配備することができる。また、水洗排水は排水管等の排水手段により系外に排出される。これらの水洗処理手段、排出管等は加熱酸化分解装置に設けても、別途独立して設けてもよい。

【0024】本発明は、上記処理工程が一連のものとして連続的かつ自動的に行われるようにかつ所望処理条件を適宜選定できるように制御装置を具備することができる。この制御装置は、通常種々の検出装置、例えば、温度、圧力、水位等のセンサーと連絡され、常に安全でしかも最適処理が行えるように構成される。

【0025】本発明における加熱酸化分解方式は高温下で排ガスを酸化分解するために短時間で処理ができるためにCVD排ガスが大量であっても除害効率が高く、また、加熱のための電気、空気、窒素、冷却用水（洗浄水を兼ねる）があれば効率よく処理できるので乾式吸着法のみよりランニングコストが低廉である。また、加熱酸化分解装置と必要により水洗部（ガス冷却、固形物除去）とNF<sub>3</sub>除害装置を直列につなぐことによって、水洗部で酸性ガスを除去し、その後加熱分解装置で分解できなかったNF<sub>3</sub>をNF<sub>3</sub>除害装置で完全に除去できる。また、導入したNF<sub>3</sub>のうち約80%が加熱酸化分解装置で除去されるためNF<sub>3</sub>除害装置への負荷が大幅に低減できる。

【0026】

【作用】本発明は、NF<sub>3</sub>クリーニングガスを含むCVDプロセス等から排出される排ガスをまず加熱酸化分解装置で処理する。加熱酸化分解装置では800℃以上1000℃以下でシラン、ジシランなどのCVD排ガスおよびNF<sub>3</sub>を酸化分解する。

【0027】次に所望により水洗部でフッ酸等の酸性ガスおよび $SiO_2$ を除去する。最後にNF<sub>3</sub>除害装置にて好ましくは300℃以上に加熱した条件でNF<sub>3</sub>を金属酸化物等と反応させ除去することによりCVD排ガスおよびNF<sub>3</sub>クリーニング排ガスを完全に分解除去することができる。

【0028】

【実施例】本発明の具体的実施例を図1に従って説明するが、本発明はこれにより限定されない。

【0029】図1は、本発明法に使用される処理装置の一例を示し、本発明のNF<sub>3</sub>排ガス処理装置1は、加熱酸化分解装置2とNF<sub>3</sub>除害装置3とから構成される。加熱酸化分解装置2は、CVD装置からのCVD排ガスを導入する排ガス流入管4、排ガス酸化を調整するための窒素を導入するための窒素流入管5および排ガス中の

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加熱酸化分解性物質を酸化するための酸素を供給するための空気流入管6を同心状に構成した3層構造のガス導入部7と、ガス導入部から放出されるこれら混合ガス中の排ガスを加熱酸化分解するための熱源であるセラミックヒータ8を外壁に有すると共に熱電対9、10を配備した温度制御されている反応部11と、反応部11にて生成した加熱酸化分解生成物を含む処理ガスを冷却水12にて水洗処理するための水洗部13とF<sub>2</sub>、SiF<sub>4</sub>等の可溶性物質、SiO<sub>2</sub>等を含む排水を系外に排出する排水管14から構成される。

【0030】NF<sub>3</sub>除害装置3は、加熱酸化分解装置2の後段に設けられ供給管15を介して水洗処理された処理ガスが該NF<sub>3</sub>除害装置3に導入される。該NF<sub>3</sub>除害装置3は、導入されたNF<sub>3</sub>等の除害すべきガスを除害処理する金属酸化物等を充填したものであり、ここを\*

\*通過させることにより排ガスを浄化かつ無害化することができ、これを配備された排気管16より、排出する。尚、17~19は排ガス、加熱酸化分解・水洗処理されたガス、触媒処理されたガスの各サンプリング管A、B、Cである。

【0031】

【実験例】図1に示した装置を用いて処理試験を行った。NF<sub>3</sub>とSiH<sub>4</sub>を含む排ガス量は40L/分、加熱酸化分解装置の処理条件は反応温度900℃、N<sub>2</sub>10L/分、酸化用空気20L/分、冷却水4L/分とした。NF<sub>3</sub>除害装置の反応温度を300℃とした。その結果を表1に示す。表中、A、B、Cは、サンプリングした管を示す。

【0032】

【表1】

表-1

単位：ppm

	NF <sub>3</sub>			SiH <sub>4</sub>		
	A	B	C	A	B	C
1 時間	5100	950	< 10	3000	< 5	< 5
2 時間	5000	850	< 10	2800	< 5	< 5
3 時間	5000	1000	< 10	3100	< 5	< 5
4 時間	5000	850	< 10	3000	< 5	< 5

【0033】表1に示したように加熱酸化分解装置でSiH<sub>4</sub>は除去でき、NF<sub>3</sub>も80~83%除去できる。残留したNF<sub>3</sub>を後段のNF<sub>3</sub>除害装置で処理することにより、CVDから発生する排ガスを完全に除害できる。

【0034】

【発明の効果】本発明の排ガス処理方法により、従来行われていた吸着法に比べてランニングコストの低減および有害ガスの高効率での除去を可能にした。また、本発明ではCVD排ガスとクリーニング排ガスが完全に分離されずに排出される枚葉式のCVD装置の排ガスを処理する場合、特に有効である。

【図面の簡単な説明】

【図1】本発明の方法が適用されるNF<sub>3</sub>排ガス処理装置を説明するための図である。

【符号の説明】

- 1 NF<sub>3</sub>排ガス処理装置
- 2 加熱酸化分解装置
- 3 NF<sub>3</sub>除害装置
- 4 排ガス流入管
- 5 窒素流入管
- 6 空気流入管
- 7 ガス導入部
- 8 セラミックヒータ
- 9 熱電対
- 10 熱電対

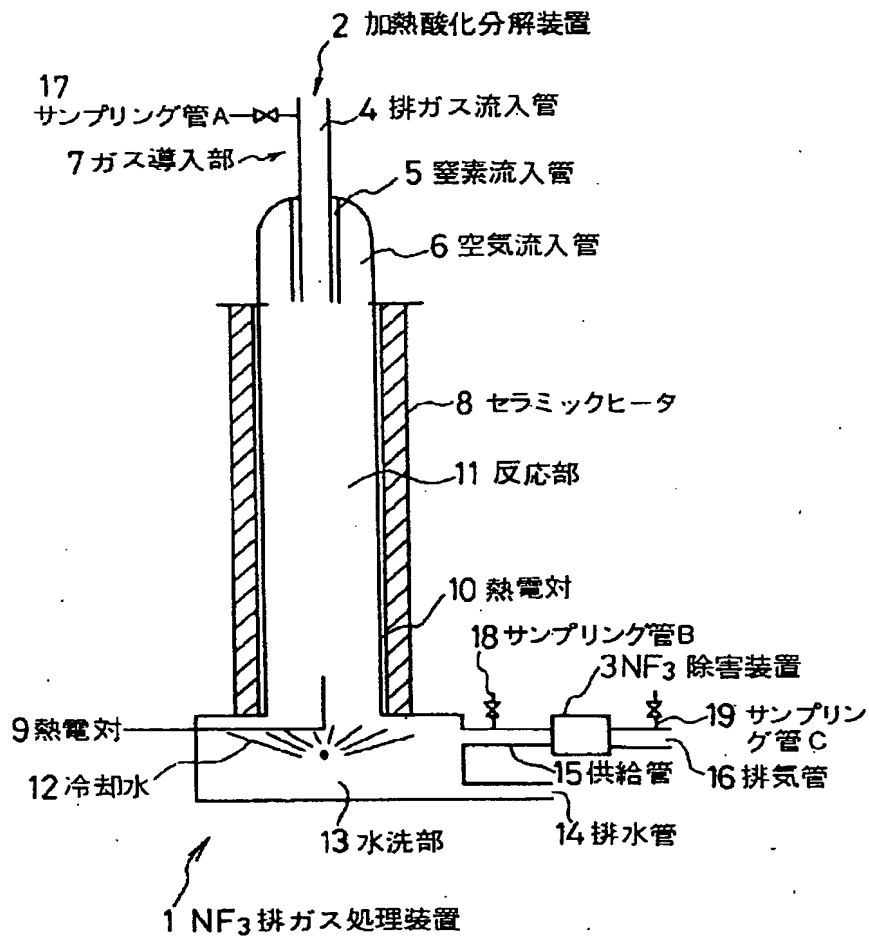
(5)

特開平4-290523

12 冷却水  
13 水洗部  
14 排水管  
15 供給管

16 排気管  
17 サンプリング管A  
18 サンプリング管B  
19 サンプリング管C

【図1】



Japanese Patent Laid-Open No. 4-290523

[Title of the Invention]

NF<sub>3</sub> Waste Gas Treatment Method and System

[Abstract]

[Object]

To provide an NF<sub>3</sub> waste gas treatment method and a system to which this method is applied, wherein its running cost is low and its removal rate of toxic gas is high.

[Solving Means]

An NF<sub>3</sub> waste gas treatment system 1 according to this invention comprises a thermal oxidative decomposition apparatus 2 and an NF<sub>3</sub> detoxing apparatus 3. In this system, waste gas from a waste gas inlet pipe 4, nitrogen from a nitrogen inlet pipe 5, and air from an air inlet pipe 6 are discharged into a reaction part 11 of the thermal oxidative decomposition apparatus 2 to cause the waste gas to be heated, oxidized and decomposed, whereby most of NF<sub>3</sub> is oxidized and decomposed, and the gas to be treated containing thermal oxidative decomposable products produced is washed with cooling water 12 at a water washing part 13. Then the waste water containing soluble substances such as F<sub>2</sub>, SiF<sub>4</sub>, SiO<sub>2</sub>, etc. is discharged out of the system and, at the same time, the gas washed with water is fed into the

NF<sub>3</sub> detoxing apparatus 3, and not-yet oxidized NF<sub>3</sub> etc. of the gas is removed and treated by using metal oxide etc. to purify and make non-toxic the waste gas.

[Claims]

[Claim 1]

An  $\text{NF}_3$  waste gas treatment method characterized in that waste gas containing  $\text{NF}_3$  is subjected to a thermal oxidative decomposition treatment and  $\text{NF}_3$  remaining in the gas treated is detoxed.

[Claim 2]

An  $\text{NF}_3$  waste gas treatment system characterized by comprising an apparatus for subjecting a waste gas containing  $\text{NF}_3$  to a thermal oxidative decomposition treatment and a detoxing apparatus for detoxing  $\text{NF}_3$  remaining in the gas treated.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to a method and apparatus for purifying and detoxing  $\text{NF}_3$  waste gas generated in a manufacturing process of a semiconductor or liquid crystal.

[0002]

[Prior Art]

CVD waste gas requires to be treated because it contains a great amount of unreacted process gas and harmful ingredients generated in its decomposing action.

[0003]

In addition,  $\text{NF}_3$  used for cleaning in CVD contains unreacted  $\text{NF}_3$  acting as a cleaning waste gas,  $\text{SiF}_4$  generated through reaction, etc. Therefore,  $\text{NF}_3$  is required to be treated and be non-toxic.

[0004]

Conventionally, a CVD waste gas has been treated by an absorbing method performed by a wet-type scrubber, an adsorption method performed with a solid adsorbing agent, a combustion method, and the like are applied. In addition,  $\text{NF}_3$  has been treated with a combination of the wet-type absorption process or thermal decomposition and adsorption process.

[0005]

The wet-type absorption process sometimes has a low removal rate of harmful gas. Although the adsorption method has a high removal rate, it is requested that an adsorption agent or a decomposing agent is replaced. This results in that its running cost becomes high. Although the combustion method is effective for the CVD waste gas treatment where a combustible gas is treated, it is not possible to treat the cleaning gas.

[0006]

This invention realizes a low running cost and a high removal rate of a toxic gas.

[0007]

[Means for Solving the Problems]

This invention provides a treatment method described below (1) and a treatment apparatus described below (2), and so the aforesaid problems can be solved.

[0008]

(1) An  $\text{NF}_3$  waste gas treatment method characterized in that waste gas containing  $\text{NF}_3$  is subjected to a thermal oxidative decomposition treatment and  $\text{NF}_3$  remaining in the gas treated is detoxed.

(2) An  $\text{NF}_3$  waste gas treatment system characterized by comprising an apparatus for subjecting a waste gas containing  $\text{NF}_3$  to a thermal oxidative decomposition treatment and a detoxing apparatus for detoxing  $\text{NF}_3$  remaining in the gas treated.

[0009]

A waste gas containing  $\text{NF}_3$  i.e., an  $\text{NF}_3$  waste gas (hereinafter referred to as a waste gas) in this invention may be any type of gas containing  $\text{NF}_3$ . For example, the  $\text{NF}_3$  waste gas means a waste gas used in an apparatus using a cleaning gas containing at least  $\text{NF}_3$  in a semiconductor manufacturing process. Further, the  $\text{NF}_3$  waste gas means that it includes a reactive product composed of  $\text{NF}_3$  generated as a result of cleaning treatment within the apparatus with cleaning gas and a substance to be cleaned present in the apparatus in addition to the waste gas of

the process gas. Accordingly, detoxing of  $\text{NF}_3$  in this invention involves a detoxing treatment for  $\text{NF}_3$  derivatives.

[0010]

In this invention, the waste gas is directly subjected to the thermal oxidative decomposition treatment so that most of the substantial organic constituents are formed into  $\text{CO}_2$  and water for the waste gas derived from the process gas, metal portions become metal oxide fine particles such as  $\text{SiO}_2$ , and  $\text{F}_2$ ,  $\text{NO}_x$ , etc. are generated for  $\text{NF}_3$ . Then, the treatment gas is washed with water, as desired, to remove fine particles,  $\text{F}_2$ ,  $\text{SiF}_4$ , etc. through melting or winding. Next, the treatment gas is passed through an  $\text{NF}_3$  detoxing apparatus filled with a detoxing agent to remove remained  $\text{NF}_3$ ,  $\text{NO}_x$ , etc. to provide a non-toxic treatment gas.

[0011]

This invention has an advantage in that an economic efficiency in treatment of  $\text{NF}_3$  is improved because an amount of treating not-yet oxidized  $\text{NF}_3$  at a later stage is substantially reduced by a method wherein waste gas is subjected to the thermal oxidative decomposition treatment, then the organic constituents contained in the waste gas are detoxed into water and  $\text{CO}_2$ , and most of  $\text{NF}_3$ , preferably more than 80% thereof, is oxidized.

[0012]

Detoxing agent used in this invention is not particularly limited but any type of known agent may be used, as long as it may have a function able to prevent  $\text{NF}_3$  from being discharged into an environment as it is. Specific examples of detoxing agents include a chemical detoxing agent which chemically reacts with  $\text{NF}_3$  to change a part or all of  $\text{NF}_3$  into another compound to detox  $\text{NF}_3$ , a physical detoxing agent which physically adsorbs  $\text{NF}_3$  therein and retains it, and their combined agents or the like.

[0013]

A chemical detoxing agent includes such a type that  $\text{NF}_3$  is oxidized and decomposed to be changed into  $\text{F}_2$  and  $\text{NO}_x$ , and at the same time, chemically reacts with  $\text{F}_2$ . More preferably, a chemical detoxing agent includes metals such as Iron, manganese, copper, silicon, and titanium, or their oxides.

[0014]

A physical detoxing agent includes silica, activated carbon, alumina, and molecular sieve. A form of the detoxing agent is optional. Thread-like form, powder form and other materials, for example, complex material with cellulose or the like can be used. Normally, a container provided with a flow inlet for the gas subjected to the thermal oxidative decomposition treatment and a flow outlet

for gas subjected  $\text{NF}_3$  to detoxing treatment is filled or charged with a desired amount of the agent to form a detoxing apparatus.

[0015]

It is preferable that an operation be carried out under a condition where the detoxing apparatus is kept at a temperature of  $300^\circ\text{C}$  or more when the chemical detoxing agent is used. Although it is preferable that this heating means be a heater and the like, the heating means may be implemented through heat exchanging with treated waste gas.

[0016]

Additionally, it is desirable that the treatment speed SV (a flow velocity), at the detoxing apparatus, of the gas subjected to the thermal oxidative decomposition treatment be 2000 l/h. The typical apparatus for discharging waste gas in this invention includes a CVD apparatus. The waste gas is constituted by a CVD waste gas derived from the process gas at the time of CVD processing and/or a cleaning waste gas at the time of cleaning operation.

[0017]

The process gases providing CVD waste gas are, for example, as an inorganic raw material, monosilane, disilane, dichlorosilane and etc., and as an organic raw material, TEOS (tetraethoxysilane), TMB (trimethoxyborane). These

waste gases are used in one or more kinds in single or in combination. These waste gases include some thermal oxidative decomposable products such as their unreacted product or their derivatives, reacted decomposed product, for example,  $H_2$ ,  $CO$ , alcohols such as  $C_2H_5OH$ , aldehyde such as  $CH_3CHO$ , and hydrocarbon such as  $C_2H_4$ . These waste gases are subjected to the thermal oxidative decomposition treatment to become mainly metal oxides such as  $SiO_2$ , and  $H_2O$  and  $CO_2$ . It is apparent that the thermal oxidative decomposition treatment defined herein includes a mere oxidization of substance that cannot be decomposed, that is, oxidization of unit such as hydrogen, metal or the like.

[0018]

The cleaning waste gas is composed of at least a reactive product between  $NF_2$  and substance in CVD (such as not-yet discharged CVD processed substance and the like),  $SiF_4$  and  $NF_3$  derivative, for example, a cleaning gas and a substance in CVD physically cleaned with the cleaning gas and the like.

[0019]

The cleaning gas additionally includes  $CF_4$ ,  $C_2F_6$ ,  $SF_6$  and  $ClF_3$ . A reaction condition for the thermal oxidative decomposition treatment and a waste gas feeding condition and the like in this invention are not restricted in particular. It is sufficiently applicable that the thermal

oxidative decomposable products contained in the waste gas at least under co-existence of oxygen may be heated, oxidized and decomposed. Accordingly, when the waste gas is fed into the thermal oxidative decomposition apparatus, it is concurrently required that oxygen be present at the heating and oxidization reaction part. Although a status of oxygen in its presence is optional, it is preferable that this oxygen be fed as gas containing oxygen, for example, air or the like, together with waste gas. In addition, in order to adjust the conditions for the thermal oxidative decomposition, optional gas can be mixed with it. For example, it is assumed that inert gas such as nitrogen or the like is mixed. It is preferable that the oxygen be fed into a reaction part of the thermal oxidative decomposition apparatus under a three-ply structure such that the nitrogen gas encloses the waste gas and oxygen encloses these gases. Furthermore, it is also preferable that a concentric three ply structure of pipes be arranged at the thermal oxidative decomposition apparatus as a feeding part of these gases.

[0020]

In addition, although the heating means in the thermal oxidative decomposition apparatus is arbitrary, it is preferably desirable to employ a heating system with a heater in which temperature can be electrically controlled

as described above and it is normally possible to arrange it within the wall of the reaction part. Additionally, a temperature at the reaction part is preferably in a range of 800 to 1000°C.

[0021]

In this invention, it is possible that the waste gas which is subjected to the thermal oxidative decomposition treatment is transferred as it is to a detoxing apparatus for detoxing  $\text{NF}_3$  according to its composition or transferred to the detoxing apparatus after undergoing another optional treatment.

[0022]

In particular, it is preferable in this invention to contact the waste gas subjected to thermal oxidative decomposition treatment with water, that is, to apply the waste gas to the water washing process. With this arrangement, it is possible to remove metal oxide fine particles such as  $\text{SiO}_2$  generated by the decomposition treatment through their enclosing operation, remove water soluble compound such as  $\text{SiF}_4$  and  $\text{F}_3$  through their solubility, cool the treated gas and the like. Although this method for water washing process is optional, it is preferable that it should be contacted with the process gas in its atomized state.

[0023]

The gas washed with water and then subjected to  $\text{NF}_3$  detoxing treatment can be discharged into the environment or can be treated with another optional treatment as desired, for example, treated with a known adsorption process and the like. The optional gas discharging means, for example, the gas discharging pipe or the like can be arranged at the detoxing apparatus. In addition, discharging of washed water out of the system is performed by a water discharging means such as a water discharging pipe. The water washing means and the discharging pipe or the like may be arranged at the thermal oxidative decomposition apparatus or separately installed in its independent manner.

[0024]

This invention can be provided with a control apparatus operated in such a way that a series of the aforesaid treatment steps may be performed continuously and automatically and that a desired treatment condition can be properly selected. This control apparatus is usually communicated with various kinds of detector apparatuses, for example, a temperature sensor, pressure sensor, water-level sensor and the like and constructed such that a safe and optimum treatment is carried out.

[0025]

Since the thermal oxidative decomposition system in

this invention oxidizes and decomposes waste gas under a high temperature and its treatment can be performed within a short period of time, even if a large amount of CVD waste gas is present, a more efficient treatment can be carried out. Furthermore, electricity, air, nitrogen and cooling water (also acting as cleaning water) for heating operation are present, the treatment can be performed with high efficiency. As a result, a less expensive running cost than that of applying only a dry adsorption method is attained. In addition, the thermal oxidative decomposition apparatus, a water washing part (gas cooling and solid material removing) as required and an  $\text{NF}_3$  detoxing apparatus are connected in series, whereby acid gas is removed at the water washing part and thereafter  $\text{NF}_3$  that could not be decomposed with the thermal decomposition apparatus can be removed completely by the  $\text{NF}_3$  detoxing apparatus. In addition, about 80% of the fed  $\text{NF}_3$  is removed by the thermal oxidative decomposition apparatus, so that a load on the  $\text{NF}_3$  detoxing apparatus can be substantially reduced.

[0026]

[Operation]

This invention treats at first the waste gas including  $\text{NF}_3$  cleaning gas discharged from the CVD process and the like with the thermal oxidative decomposition

apparatus. The thermal oxidative decomposition apparatus oxidizes and decomposes at a temperature more than 800°C and less than 1000°C CVD waste gases such as silane and disilane, and  $\text{NF}_3$ .

[0027]

Then, an acid gas such as fluoric acid and  $\text{SiO}_2$  are removed at the water washing part as desired. Lastly,  $\text{NF}_3$  is made to react with metal oxides at the  $\text{NF}_3$  detoxing apparatus under a condition of heated state of preferably 300°C or more and removed, whereby the CVD waste gas and the  $\text{NF}_3$  cleaning waste gas can be completely decomposed and removed.

[0028]

[Preferred Embodiment]

Referring to Fig. 1, a practical preferred embodiment of this invention will be described as follows. This invention is not limited to this preferred embodiment.

[0029]

Fig. 1 shows one example of the treatment system used in this invention, wherein an  $\text{NF}_3$  waste gas treatment system 1 of this invention includes a thermal oxidative decomposition apparatus 2 and an  $\text{NF}_3$  detoxing apparatus 3. The thermal oxidative decomposition apparatus 2 includes a gas feeding part 7 of a three-ply structure having concentrically arranged a waste gas inlet pipe 4 for

feeding a CVD waste gas from a CVD apparatus, a nitrogen inlet pipe 5 for feeding nitrogen for adjusting oxidization of a waste gas and an air inlet pipe 6 for supplying oxygen to oxidize the thermal oxidative decomposable products in the waste gas. The thermal oxidative decomposition apparatus 2 includes a reaction part 11 having at its outer wall a ceramic heater 8 acting as a heat source for subjecting the waste gas in these mixed gases released from the gas feeding part to heating, oxidizing and decomposing treatment and having thermocouples 9, 10 to control its own temperature; a water washing part 13 for washing with water the gas to be treated including the thermal oxidative decomposable products generated at the reaction part 11 by cooling water 12; and a discharging pipe 14 for discharging water containing soluble substances such as  $F_2$ , and  $SiF_4$ , and  $SiO_2$  outside the system.

[0030]

The  $NF_3$  detoxing apparatus 3 is arranged at the rear stage of the thermal oxidative decomposition apparatus 2 and the treated gas washed with water is fed into the  $NF_3$  detoxing apparatus 3 through a supply pipe 15. The  $NF_3$  detoxing apparatus 3 is filled with metal oxide used for detoxing gas such as fed  $NF_3$ . The waste gas can be purified and detoxed by passing through the  $NF_3$  detoxing apparatus 3, and then discharged through the arranged gas discharging

pipe 16. Reference numerals 17 to 19 each denotes the sampling pipes A, B and C for sampling the waste gas, gas subjected to heating, oxidizing, decomposing and to water-washing, and gas treated with catalyst.

[0031]

[Experimental Example]

A treatment test was carried out with the apparatus shown in Fig. 1. An amount of waste gas including  $\text{NF}_3$  and  $\text{SiH}_4$  was 40L/min. The treatment condition for the thermal oxidative decomposition apparatus, was set such that a reaction temperature was  $900^\circ\text{C}$ ,  $\text{N}_2$  10 L/min., air for oxidation 20 L/min. and the cooling water 4L/min. A reaction temperature of the  $\text{NF}_3$  detoxing apparatus was set to  $300^\circ\text{C}$ . The result will be indicated in Table 1. A, B and C in this table denote sampled pipes.

[0032]

Table-1

Unit: ppm

	$\text{NF}_3$			$\text{SiH}_4$		
	A	B	C	A	B	C
1 hour	5100	950	<10	3000	<5	<5
2 hours	5000	850	<10	2800	<5	<5
3 hours	5000	1000	<10	3100	<5	<5
4 hours	5000	850	<10	3000	<5	<5

[0033]

As indicated in Table-1,  $\text{SiH}_4$  can be removed by the thermal oxidative decomposition apparatus, and  $\text{NF}_3$  can also be removed by about 80 to 83%. The residual  $\text{NF}_3$  is treated with the  $\text{NF}_3$  detoxing apparatus at a rear stage, whereby the waste gas generated from CVD can be completely detoxed.

[0034]

[Effect of the Invention]

The waste gas treatment method of this invention reduces the running cost as compared with that of the adsorption process of the prior art and further attains a high efficient removal of a harmful gas. In addition, this invention is quite effective when the waste gas of the CVD apparatus operated in a sheet-like manner is treated, where a CVD waste gas and a cleaning waste gas are not separated completely and discharged.

[Brief Description of the Drawing]

[Fig. 1]

This is an explanatory figure of a  $\text{NF}_3$  waste gas treatment system to which the method of the present invention is applied.

[Description of the Reference Numerals]

- 1  $\text{NF}_3$  waste gas treatment system
- 2 Thermal oxidative decomposition apparatus
- 3  $\text{NF}_3$  detoxing apparatus
- 4 Waste gas inlet pipe

- 5 Nitrogen inlet pipe
- 6 Air inlet pipe
- 7 Gas inlet part
- 8 Ceramic heater
- 9 Thermocouple
- 10 Thermocouple
- 12 Cooling water
- 13 Water washing part
- 14 Discharging pipe
- 15 Supply pipe
- 16 Discharging pipe
- 17 Sampling pipe A
- 18 Sampling pipe B
- 19 Sampling pipe C

DECLARATION

I, Kazuhiro ISHII , a national of Japan,  
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do hereby solemnly and sincerely declare:-

- 1) THAT I am well acquainted with the Japanese language  
and English language, and
- 2) THAT the attached is a full, true, accurate and  
faithful translation into the English language made  
by me of Japanese Patent Application No. 9-4349.

The undersigned declares further that all  
statements made herein of his own knowledge are true and  
that all statements made on information and belief are  
believed to be true; and further that these statements  
were made with the knowledge that willful false statements  
and the like so made are punishable by fine or imprisonment,  
or both, under section 1001, of Title 18 of the United  
States Code and that such willful false statements may  
jeopardize the validity of the application or any patent  
issuing thereon.

Signed this 29<sup>th</sup> day of December , 2005 .

  
Kazuhiro ISHII

KANNO EXHIBIT 1001  
Rossin v. Kanno  
Contested Case 105,402

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[Title of the Invention]  
PROCESS FOR TREATING FLUORINE  
COMPOUND-CONTAINING GAS  
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[Title of Article] Drawings ..... 1

[Title of Article] Abstract ..... 1

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[Proof Required or not] yes

[Title of Document]      Description

[Title of the Invention]      PROCESS FOR TREATING FLUORINE  
COMPOUND-CONTAINING GAS

[Claims]

5    [Claim 1]

A process for treating a fluorine compound-  
containing gas, characterized by containing a step of  
contacting a gas stream containing at least one of a  
compound including two or more carbon atoms and fluorine  
10 atom(s), or a compound containing nitrogen atom(s) and  
fluorine atom(s) with a catalyst containing at least one  
of alumina, titania, silica and zirconia at a  
temperature of about 400 to 800°C in the presence of an  
effective amount of water vapor to convert the F in the  
15 gas stream to HF.

[Claim 2]

The process according to Claim 1, wherein the  
fluorine compound-containing gas includes a compound of  
C and F having two or more carbon atoms, or a compound  
20 of N and F.

[Claim 3]

The process according to Claim 1, wherein the  
catalyst further contains at least one component  
selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni.

25    [Claim 4]

A catalyst for decomposing fluorine compounds

by treating a gas stream containing at least one of a compound of C and F having two or more carbon atoms, or a compound of N and F, said catalyst comprising alumina and titania, wherein the alumina is contained 75% by weight or more and 98% by weight or less, and the titania is contained 25% by weight or less and 2% by weight or more.

[Claim 5]

The catalyst according to Claim 4, wherein the catalyst further contains at least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B.

[Claim 6]

The catalyst according to Claim 5, wherein the catalyst contains one or more oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in an amount of 0.1% by weight to 10% by weight based on the main weight of the aluminatitania catalyst.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a process for efficient decomposition treatment of a gas containing fluorine compounds such as  $C_2F_6$ , etc. at a low temperature and a catalyst material.

[0002]

[Prior Art]

Fluorine compound gases such as  $C_2F_6$ , etc. are used in a large amount as a semiconductor etchant, a semiconductor cleaner, etc. However, it was found that these compounds, once discharged into the atmosphere, turn into warming substances causing global warming. Post-treatment of these compounds after their use would be subject to a strict control in the future.

[0003]

By the way, gases such as  $C_2F_6$ , etc. have fluorine (F) in a large amount as a molecular constituting element. The fluorine is the highest in electronegativity among all the elements and forms chemically very stable substances. Particularly,  $C_2F_6$  and the like are strong in intramolecular force and substances poor in reactivity. From these properties, a high temperature is necessary for decomposition and a large amount of energy is consumed therefor. Further, the decomposition reaction at the high temperature produces gases such as hydrogen fluoride, etc. which are large in corrosion rate of apparatus materials. It is thus in the current situations that no appropriate processes for such decomposition treatment are not available yet.

[0004]

As the decomposition treatment processes, there is proposing a combustion technology at a high temperature. But, according to this process, since a large amount of fuel is used, the energy efficiency is

low. In addition, there is a problem of damage of furnace wall caused by halogen compounds produced by combustion at 1000°C or higher. Therefore, it is necessary a technology which can decompose at lower  
5 temperatures.

[0005]

As to the catalyst, JP-B-6-59388 discloses a  $\text{TiO}_2\text{-WO}_3$  catalyst for decomposition of organic halogen compounds. The catalyst contains 0.1 to 20% by weight  
10 of W on the basis of  $\text{TiO}_2$  (i.e. 92% to 99.96% of Ti by atom and 8 to 0.04% by atom of W) and had a decomposition rate of 99% at 375°C for a duration of 1,500 hours in treatment of  $\text{CCl}_4$  in ppm order. Among organic halogen compounds, influences as catalyst poison are found not  
15 only in Cl but also in F, the latter is greater than the former. JP-B-6-59388 suggests that organic halogen compounds having a single carbon atom, such as  $\text{CF}_4$ ,  $\text{CCl}_2\text{F}_2$ , etc. can be decomposed, but shows no examples of decomposition results of fluorine compounds. Further,  
20 generally speaking, organic halogen compounds having 2 carbon atoms are less decomposable than those having a single carbon atom.

JP-A-7-80303 discloses another  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-WO}_3$  catalyst for decomposition of fluorine compound gases.  
25 The catalyst is directed to combustion-decomposition of CFCs (chlorofluorocarbons) and has a decomposition rate of 98% for a duration of 10 hours in treatment of CFC-115 ( $\text{C}_2\text{ClF}_5$ ) by combustion-decomposition reaction at

600°C. The disclosed process needs addition of hydrocarbons such as n-butane, etc. as a combustion aid, resulting in a higher treatment cost. Decomposition of compounds consisting only of carbon and fluorine such as  
5 C<sub>2</sub>F<sub>6</sub>, etc. are much less decomposable than CFC-115, but no examples of decomposition results of such compounds are shown therein.

[0006]

[Problem to be Solved by the Invention]

10 An object of the present invention is to provide a process for efficient decomposition treatment of a gas containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound having nitrogen atom(s) and fluorine atom(s) at  
15 a low temperature, and a catalyst therefore.

[0007]

[Means for Solving Problem]

The present inventors have studied decomposition treatment processes which are possible to  
20 decompose fluorine compound-containing gas at low temperatures with high efficiency and hardly provide corrosion of the apparatus by hydrogen fluoride freed as a decomposition product, and as a result, the present invention is attained.

25 [0008]

That is, it was found that by contacting a gas stream containing at least one of a compound having two or more carbon atoms and fluorine atom(s), or a compound

having nitrogen atom(s) and fluorine atom(s) with a catalyst for decomposing specific fluorine compounds at about 400 to about 800°C in the presence of an efficient amount of water vapor, the fluorine in the gas stream  
5 can be converted to HF. As the decomposing catalyst, it is possible to use a catalyst which contains at least one kind selected from alumina, titania, silica and zirconia.

[0009]

10 As the fluorine compounds, there can be used those having C and F with two or more carbon atoms such as C<sub>2</sub>F<sub>6</sub>, etc., those having N and F such as NF<sub>3</sub>, etc.

[0010]

Further, it was found that when at least one  
15 component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni is added to the catalyst, it was possible to decompose the fluorine compound-containing gas with higher activity. These catalysts contains alumina, titania, silica, zirconia and oxide or oxides of at  
20 least one component selected from Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P and B in the form of a mixture or composite oxide. In the case of the catalyst containing alumina and titania, when alumina is 75% by weight or more and 98% by weight or less and titania is 25% by  
25 weight or less and 2% by weight or more, the effects are very great. Further, when the oxide of Si, Mg, Zr, W, Sn, Ce, Mn, Bi, Ni, P, and B is contained 0.1 to 10% by weight based on the main weight of the

catalyst, the effects are great.

[0011]

As a result of various studies for developing decomposition catalysts for fluorine compound-containing gas, it was found that it is necessary to contain a metallic component for forming a bond to fluorine with a suitable strength. Particularly, in the case of a compound containing carbon and fluorine, since the molecule per se is stable, it was found that a catalyst containing a metallic component having a large fluoride forming enthalpy shows a high decomposition activity. When a too stable bond is formed, the activity lowers gradually because of non-release of the fluoride from the catalyst surface. On the other hand, when the bonding strength is too weak, a sufficient decomposition rate cannot be obtained. The gases used in the present invention such as  $C_2F_6$  or the like are substances which have a strong intramolecular force and poor reactivity. In order to combust these gases, the temperature of 1500 to 2000°C is said to be necessary. We have found that the gases used in the present invention can be decomposed by even using alumina, titania, silica and zirconia singly as a catalyst, and in order to obtain higher decomposition rate, it is preferable to use a catalyst containing alumina and titania. The alumina seems to function for drawing the fluorine compound to the catalyst and the titania seems to function for separating the fluorine compound from the catalyst

surface.

[0012]

The oxides of Si, Mg, Zr, W, Sn, Ce, Mn, Bi and Ni seem to exhibit synergistic effects with alumina, 5 titania, silica and zirconia. Further, the titania in the catalyst seems to contribute to the stabilitation.

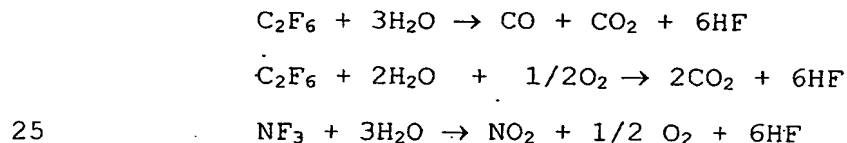
[0013]

In the decomposition treatment process of the fluorine compound-containing gas of the present 10 invention, it was found that the fluorine compound such as C<sub>2</sub>F<sub>6</sub> or the like can be diluted with an inert gas. By diluting the concentration of the fluorine compound, the load for the catalyst is reduced, resulting in maintaining the decomposition activity for a long period 15 of time. As the diluting gas, it is possible to use an inert gas such as Ar, N<sub>2</sub>, He or the like.

[0014]

The fluorine-containing compounds used in the present invention are PFC (perfluorocompounds) such as 20 C<sub>2</sub>F<sub>6</sub>, NF<sub>3</sub>, etc. or FFC (fully fluorocompounds). Typical reactions can be shown below.

[0015]



It is desirable to add these fluorine compounds so as to make the amount of hydrogen atoms in

the gas to be treated at least equal to the amount of fluorine atoms contained in the fluorine compound. By this, F in the compound becomes HF, and F in the decomposition products changes into hydrogen halide  
5 which is easy for after-treatment. As a hydrogen source, there can be used steam, hydrogen, a hydrocarbon, etc. In the case of using a hydrocarbon, the hydrocarbon can be combusted on the catalyst, thereby effectively reducing the heat energy to be  
10 supplied.

[0016]

By adding an oxidizing gas such as oxygen, etc. to the reaction gas, oxidation reaction of CO can be carried out at the same time. When the oxidation  
15 reaction of CO is incomplete, the decomposition product gas is brought into contact with the CO oxidizing catalyst, after removal of HF from the decomposition product gas, to convert CO to CO<sub>2</sub>.

[0017]

20 By using the catalyst of the present invention, flons such as C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, C<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>ClF<sub>5</sub>, etc., substitute flons such as HFC 134a, etc. and compounds such as SF<sub>6</sub>, etc. can be decomposed. Further, Cl in the compounds in the case of treating chlorine compounds is  
25 converted to HCl.

[0018]

The reaction temperature used in the present invention is preferably about 200° to about 800°C. Above

the higher temperatures, a higher decomposition rate can be obtained, but the catalyst will be rapidly deteriorated, and also the corrosion rate of apparatus structural materials will be abruptly increased, whereas  
5 below the lower temperature, the decomposition rate will be lowered.

As the step of neutralizing and removing the formed HF, washing by spraying an alkaline solution is efficient and preferable because of less occurrence of  
10 clogging in pipes due to crystal deposition, etc. Bubbling of the decomposition product gas through the alkaline solution or washing with the alkaline solution through a packed column may be used.

[0019]

15 As the raw material for aluminum (Al) for preparing the catalyst of the present invention,  $\gamma$ -alumina and a mixture of  $\gamma$ -alumina and  $\delta$ -alumina can be used. Particularly preferable method is to use boehmite, etc. as a raw material for Al to form an oxide  
20 through final firing.

[0020]

As the raw material for titanium (Ti) for preparing the catalyst of the present invention, there can be used titanium sulfate, titania sol, titanium  
25 slurry, etc.

[0021]

Further, as raw materials for the third metallic components such as silica (Si), magnesium (Mg),

zirconium (Zr), etc., their various nitrates, ammonium salts, chlorides, etc. can be used.

[0022]

5 The catalyst of the present invention can be prepared by any of ordinary procedures for preparing catalysts, such as a precipitation method, an impregnation method, a kneading method, etc.

[0023]

10 The catalyst of the present invention can be used as such or upon molding into a granular form, a honeycomb form, etc. by a desired molding procedure such as extrusion molding, tableting, tumbling granulation, etc., or as a coating on ceramic or metallic honeycombs or plates.

15 [0024]

The fluorine compound-containing gas treating process of the present invention can decompose the fluorine compounds in a lower temperature than other treating processes.

20 [0025]

In the case of treating fluorine compound-containing gas, there arises a problem of corrosion of apparatus materials caused by the acid component such as HF, etc. produced by decomposition. According to the  
25 present invention, since the temperature used is relatively low, the corrosion rate is slow, resulting in unnecessary for maintenance of the apparatus.

[0026]

The apparatus for practicing the fluorine compound-containing gas treating process of the present invention requires only a catalytic reactor for decomposing the fluorine compounds and an apparatus for  
5 neutralizing and removing acid components in the decomposition product gas, so that the apparatus can be minimized.

[0027]

[Mode for Carrying Out the Invention]

10 The present invention will be described in detail below, referring to Examples which are not limitative of the present invention.

[0028]

Fig. 1 shows an example of using the  
15 decomposition treatment process of the present invention for a cleaning step in a plasma CVD apparatus in the semiconductor production process.

[0029]

The plasma CVD apparatus is an apparatus for  
20 vapor depositing a  $\text{SiO}_2$  film on a semiconductor wafer surface. Since the  $\text{SiO}_2$  film tends to deposit on the entire interior surfaces of the apparatus, and thus it is necessary to remove  $\text{SiO}_2$  depositions from unwanted surfaces. To clean the  $\text{SiO}_2$ ,  $\text{C}_2\text{F}_6$  is used. Cleaning gas  
25 containing  $\text{C}_2\text{F}_6$  is led to a CVD chamber to remove  $\text{SiO}_2$  under plasma excitation. Then, the chamber is flushed with a  $\text{N}_2$  gas, thereby diluting the concentration of  $\text{C}_2\text{F}_6$  to about 3 to 5%, followed by discharge from the chamber

at about 15 l./min.

[0030]

The discharged gas is admixed with air 3 to dilute  $C_2F_6$ . The diluted gas is further admixed with  
5 steam 4 to give a reaction gas 5, which is led to a decomposition step. The  $C_2F_6$  concentration in the reaction gas is about 0.5%. In the decomposition step, the reaction gas 5 is contacted with a  $Al_2O_3$  series catalyst at  $700^\circ C$  under the conditions of space velocity  
10 of 3000 per hour [space velocity ( $h^{-1}$ ) = reaction gas flow rate (ml/h)/catalyst volume (ml)]. In that case, the reaction gas may be heated or the catalyst may be heated by an electric oven, etc. The resulting decomposition gas 6 is led to an exhaust gas washing  
15 step, where the decomposition gas 6 is sprayed with an aqueous alkaline solution to remove acid components from the decomposition gas 6 and the resulting exhaust gas 7 freed from the acid components is discharged to the system outside. The decomposition rate of  $C_2F_6$  is  
20 obtained from the analysis data of the reaction gas 5 and the exhaust gas 7 using FID (flame ionization detector) gas chromatograph and TCD (thermal conductivity detector) gas chromatograph, and material balance at the inlet and the outlet.

25 [0031]

Hereinafter, the results obtained by examining activities of various fluorine compound decomposing catalysts are explained.

[0032]

[Example 1]

A  $C_2F_6$  gas having a purity of 99% or more was diluted with air, and further admixed with steam to  
5 prepare a reaction gas. Steam for the admixture was prepared by feeding pure water into a reactor tube from the top at a flow rate of 0.11 ml/min. by a microtube pump and gasified. The reaction gas had a  $C_2F_6$  concentration of about 0.5%. Then, the reaction gas was  
10 brought into contact with various catalysts heated to 700°C in the reactor tube at a space velocity of 3,000  $h^{-1}$ .

[0033]

The reactor tube is a reactor tube  
15 manufactured by Inconel and having an inner diameter of 19 mm, where a catalyst bed is fixed at the center of the reactor tube and had an Inconel-made thermowell for a thermo couple, 3 mm in outer diameter, inside the catalyst bed. Decomposition product gas discharged from  
20 the catalyst bed was bubbled through an aqueous sodium chloride solution and then discharged as an exhaust gas.  $C_2F_6$  decomposition rate was calculated by the following equation using FID gas chromatograph and TCD gas chromatograph:

25 [0034]

[Expression 1]

$$\text{Decomposition rate} = 1 - \frac{\text{Concentration of discharged fluorine compound}}{\text{Concentration of fed fluorine compound}} \times 100 (\%)$$

[0035]

Hereinafter, preparation methods of various catalysts used for the tests under the above-mentioned conditions are shown.

5 [0036]

Catalyst 1 :  $\text{Al}_2\text{O}_3$

Granular alumina (NKHD-24, trademark of a product commercially available from Sumitomo Chemical Co., Ltd., Japan) was pulverized, sieved to obtain a  
10 fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing (or calcining) at 700°C for 2 hours, and subjected to the tests.

[0037]

Catalyst 2 :  $\text{TiO}_2$

15 Granular titania (CS-200-24, trademark of a product commercially available from Sakai Chemical Industry Co., Ltd., Japan) was pulverized, sieved to obtain a fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours,  
20 and subjected to the tests.

[0038]

Catalyst 3 :  $\text{ZrO}_2$

200 g of zirconyl nitrate was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The  
25 resulting powders were placed in a mold and compression

molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain zirconia grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

5 [0039]

Catalyst 4 : SiO<sub>2</sub>

Granular silica (CARIACT-10, trademark of a product commercially available from Fuji Silysia Co., Ltd., Japan) was pulverized and sieved to obtain a  
10 fraction of 0.5 - 1 mm grain sizes, followed by drying at 120°C for 2 hours, firing at 700°C for 2 hours, and subjected to the tests.

[0040]

Catalyst 5 : TiO<sub>2</sub>-ZrO<sub>2</sub>

15 Granular titania (CS-200-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders was admixed with 78.3 g of zirconyl nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2  
20 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

25 [0041]

Catalyst 6 : Al<sub>2</sub>O<sub>3</sub>-MgO

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting

powders were admixed with 56.4 g of magnesium nitrate and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting  
5 powders were placed into a mold and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0042]

10 Catalyst 7 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

Granular alumina (NKHD-24) was pulverized to grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 17.4 g of dried powders of a metatitanic acid slurry and kneaded while adding pure  
15 water thereto. After the kneading, the kneaded mixture was dried at 120°C for 2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain  
20 grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0043]

Catalyst 8 : Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

Granular alumina (NKHD-24) was pulverized to  
25 grain sizes of 0.5 mm and under. 100 g of the resulting powders were admixed with 13.2 g of dried powders of SiO<sub>2</sub> sol and kneaded while adding pure water thereto. After the kneading, the kneaded mixture was dried at 120°C for

2 hours and fired at 700°C for 2 hours. The resulting powders were placed in a mold and compression molded under a pressure of 500 mgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and subjected to the tests.

[0044]

Test results of the above-mentioned catalysts 1 to 8 are shown in Fig. 2.

[0045]

10 [Example 2]

In this Example, effects of addition of the third elements were examined under the same conditions as in Example 1. Individual catalysts were prepared as follows.

15 [0046]

Catalyst 9 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours, and subjected to the tests.

25 [0047]

Catalyst 10 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-ZrO<sub>2</sub>

Granular alumina (NKHD-24) was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1

mm, followed by drying at 120°C for 2 hours. Then, the dried grains were impregnated with 176 g of an aqueous 30% titanium sulfate solution. After the impregnation, the grains were dried at 250° - 300°C for about 5 hours  
5 and then fired at 700°C for 2 hours, to give Catalyst A. Then, 50 g of Catalyst A grains were impregnated with an aqueous solution of 6.7 g of zirconyl nitrate dihydrate in 90 g of H<sub>2</sub>O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2  
10 hours, and subjected to the tests.

[0048]

Catalyst 11 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-WO<sub>3</sub>

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were  
15 impregnated with 90 g of an aqueous solution of 6.5 g of ammonium paratungstate in H<sub>2</sub>O. After the impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0049]

20 Catalyst 12 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.5 g of 20 wt.% silica sol in H<sub>2</sub>O. After the impregnation, the  
25 grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

Catalyst 13 : Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SnO<sub>2</sub>

Catalyst A was prepared in the same manner as

in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 5.6 g of tin chloride dihydrate in  $H_2O$ . After the impregnation, the grains were dried at  $120^\circ C$  for 2 hours and then fired at  $700^\circ C$  for 2 hours, and subjected to the tests.

[0050]

Catalyst 14 :  $Al_2O_3-TiO_2-CeO_2$

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 10.9 g of cerium nitrate hexahydrate in  $H_2O$ . After the impregnation, the grains were dried at  $120^\circ C$  for 2 hours and then fired at  $700^\circ C$  for 2 hours, and subjected to the tests.

15 Catalyst 15 :  $Al_2O_3-TiO_2-MnO_2$

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.2 g of manganese nitrate hexahydrate in  $H_2O$ . After the impregnation, the grains were dried at  $120^\circ C$  for 2 hours and then fired at  $700^\circ C$  for 2 hours, and subjected to the tests.

[0051]

Catalyst 16 :  $Al_2O_3-TiO_2-Bi_2O_3$

25 Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.4 g of bithmus nitrate hexahydrate in  $H_2O$ . After the

impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0052]

5 Catalyst 17 :  $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-NiO}$

Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 7.3 g of nickel nitrate hexahydrate in  $\text{H}_2\text{O}$ . After the  
10 impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0053]

Catalyst 18 :  $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-BO}_4$

15 Catalyst A was prepared in the same manner as in Catalyst 10. Then, 50 g of Catalyst A grains were impregnated with 90 g of an aqueous solution of 12.0 g of ammonium borate octahydrate in  $\text{H}_2\text{O}$ . After the  
20 impregnation, the grains were dried at 120°C for 2 hours and then fired at 700°C for 2 hours, and subjected to the tests.

[0054]

Activities of the above-mentioned Catalysts 9-18 as well as that of Catalyst 1 in Example 1 are shown  
25 in Fig. 3.

[0055]

[Example 3]

In this Example, various catalysts are

prepared by changing the alumina raw material and the titania raw material, and activities are examined in the same manner as in Example 1.

[0056]

5 Catalyst 19 :  $\text{Al}_2\text{O}_3$

Boehmite powders (PURAL SB, trademark of a product commercially available from Condea Co., Ltd.) were dried at 120°C for 2 hours. 200 g of the resulting dried powders were fired at 300°C for 0.5 hour and  
10 further fired at an elevated temperature of 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and tested.

15 [0057]

Catalyst 20 :  $\text{Al}_2\text{O}_3\text{-TiO}_2$

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 200 g of the resulting dried powders were kneaded with 248.4 g of an aqueous 30% titanium sulfate  
20 solution, while adding about 200 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of  
25 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0058]

Catalyst 21 :  $\text{AlO}_3\text{-TiO}_2$

Boehmite powders (PURAL SB) were dried at  $120^\circ\text{C}$  for one hour. 200 g of the resulting dried powders were kneaded with about 100 g of an aqueous solution  
5 containing 78.6 g of 30% titania sol in pure water. After the kneading, the kneaded mixture was dried at  $120^\circ\text{C}$  for about 2 hours and then fired at  $700^\circ\text{C}$  for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of  $500\text{ kgf/cm}^2$ .  
10 The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0059]

[Example 4]

In this Example, catalysts are prepared by  
15 changing the composition of Al and Ti in Catalyst 20 in Example 3 and their activities are examined:

[0060]

Catalyst 22 :  $\text{Al}_2\text{O}_3\text{-TiO}_2$

Boehmite powders (PURAL SB) were dried at  $120^\circ\text{C}$   
20 for one hour. 100 g of the resulting dried powders were kneaded with 48.8 g of an aqueous 30% titanium sulfate solution while adding about 150 g of pure water thereto. After the kneading, the kneaded mixture was dried at  $250^\circ$  -  $300^\circ\text{C}$  for about 5 hours and then fired at  $700^\circ\text{C}$  for 2  
25 hours. The resulting powders were placed into a mold and compression molded under a pressure of  $500\text{ kgf/cm}^2$ . The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0061]

Catalyst 23 :  $\text{Al}_2\text{O}_3\text{-TiO}_2$

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were  
5 kneaded with 82.4 g of an aqueous 30% titanium sulfate solution while adding about 120 g of pure water thereto. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold  
10 and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0062]

Catalyst 24 :  $\text{Al}_2\text{O}_3\text{-TiO}_2$

15 Boehmite powders (PURAL SB) were dried at 120°C for one hour. 100 g of the resulting dried powders were kneaded with 174.4 g of an aqueous 30% titanium sulfate solution while adding about 70 g of pure water. After the kneading, the kneaded mixture was dried at 250° -  
20 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

25 [0063]

Catalyst 25 :  $\text{Al}_2\text{O}_3\text{-TiO}_2$

Boehmite powders (PURAL SB) was dried at 120°C for one hour. 100 g of the resulting dried powders were

kneaded with 392g of 30% titania sol. After the kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The resulting powders were placed into a mold and  
5 compression molded under a pressure of 500 kgf/cm<sup>2</sup>. The molded product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested.

[0064]

Activities of the above-mentioned Catalysts  
10 22-25 are examined in the same manner as in Example 1 and the results are shown in Fig. 5.

[0065]

[Example 5]

In this Example, sulfuric acid is added at the  
15 time of preparing a catalyst.

[0066]

Catalyst 26: Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>

Boehmite powders (PURAL SB) were dried at 120°C for one hour. 150 g of the resulting dried powders,  
20 58.8 g of 30% titania sol solution (CS-N, manufactured by Ishihara Sangyo Kaisha, Ltd.) and an aqueous solution of 44.8 g of 97% sulfuric acid solution diluted with 250 ml of pure water were added and kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C  
25 for about 5 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The test conditions are the same as those of Example 1,

except for changing the space velocity 1000 per hour.  
The test results were that the decomposition rate of  $C_2F_6$   
at the reaction temperature of  $650^{\circ}C$  was 80%.

[0067]

5 [Effects of the Invention]

According to the present invention, fluorine-  
containing gases such as  $C_2F_6$ ,  $NF_3$ , etc. can be subjected  
to decomposition treatment efficiently.

[Brief Description of the Drawings]

10 [Fig. 1]

A block diagram showing a treatment process  
according to one embodiment of the present invention.

[Fig. 2]

15 A graph showing performances of various  
catalysts for decomposing fluorine compounds.

[Fig. 3]

A graph showing performances of various  
catalysts for decomposing fluorine compounds.

[Fig. 4]

20 A graph showing performances of various  
catalysts for decomposing fluorine compounds.

[Fig. 5]

A graph showing performances of various  
catalysts for decomposing fluorine compounds.

25 [Description of Reference Numerals]

1 ...  $C_2F_6$ , 2 ...  $N_2$ , 3 ... air, 4 ... steam,

5 ... reaction gas, 6 ... decomposed gas, 7 ... exhaust  
gas

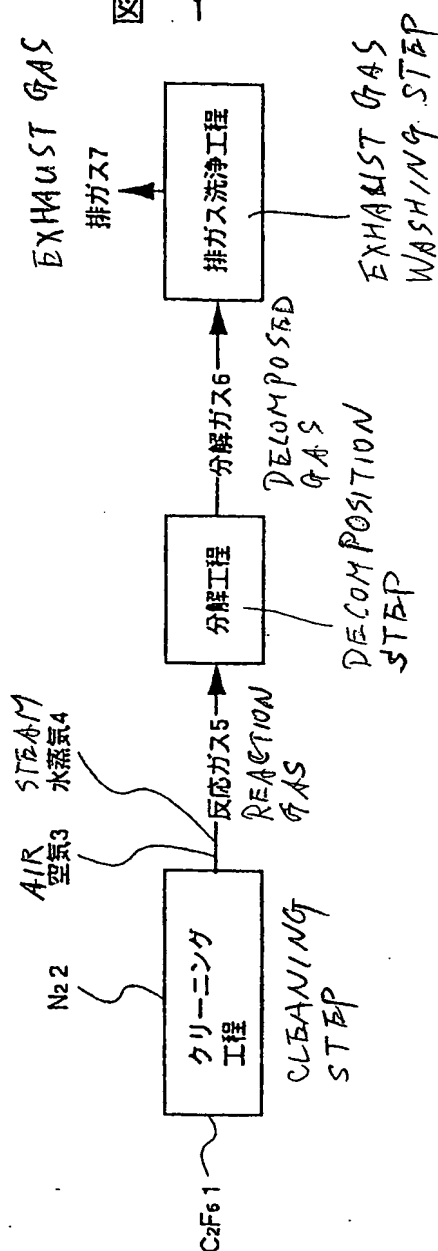
【書類名】 図面

[ Kind of Document ] Drawings

【図 1】

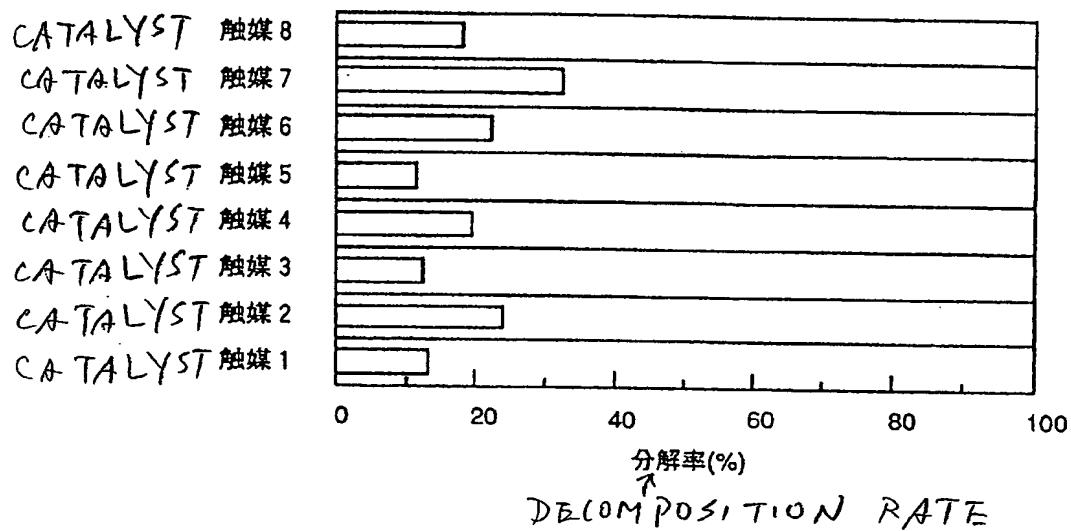
[FIG. 1]

図 1



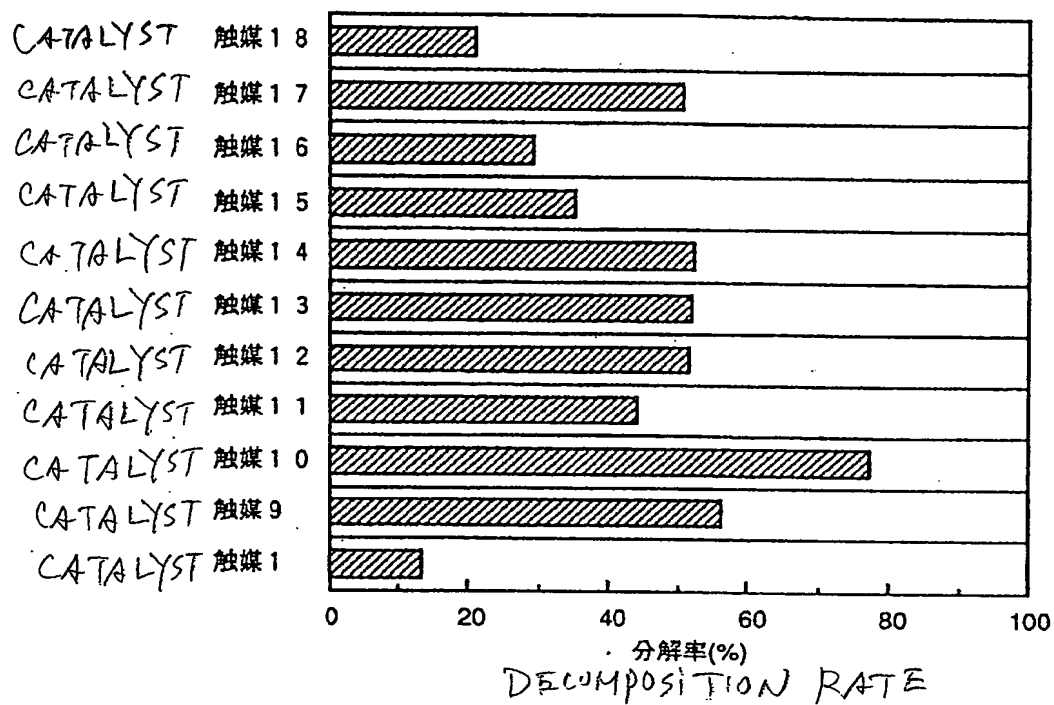
【図 2】

[Fig. 2]  
図 2



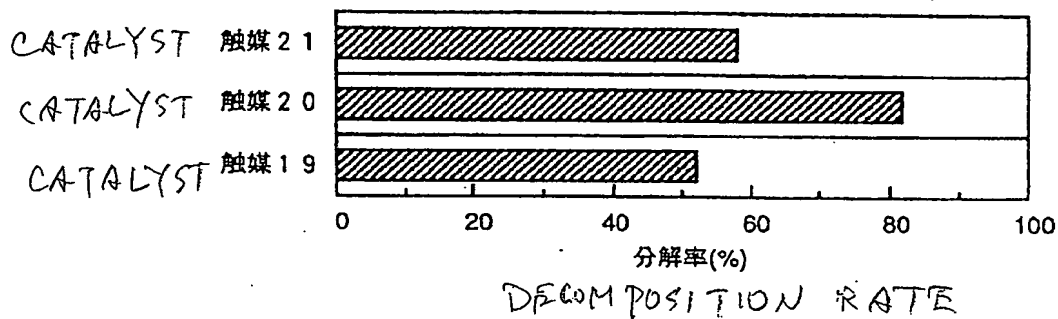
【図 3】

[ Fig. 3 ]  
図 3



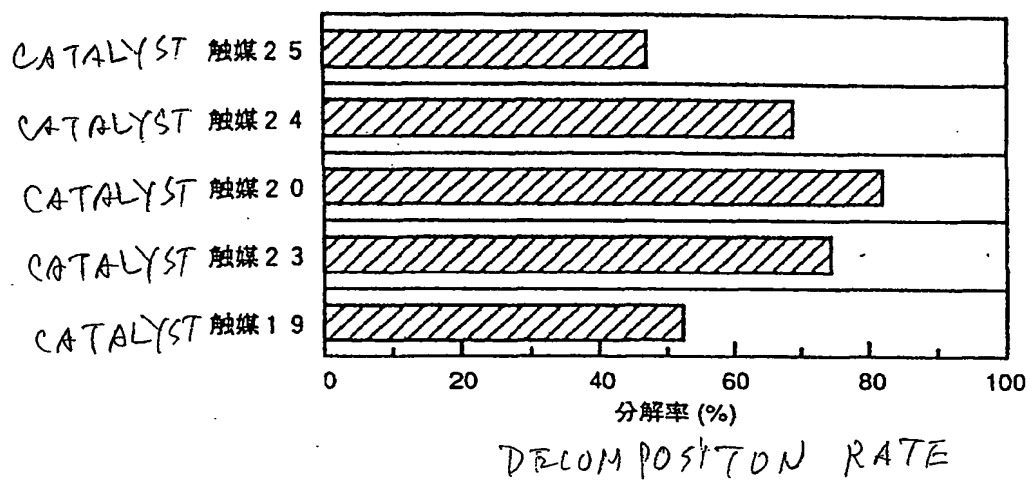
【図 4】

[ Fig. 4 ]  
図 4



【図 5】

[ Fig. 5 ]  
図 5



[Title of Document]    Abstract

[Abstract]

[Problem]    To provide a decomposition treatment process for decomposing fluorine compound-containing gas such as  $C_2F_6$  and the like efficiently and catalyst therefore.

[Solution]

A gas stream containing at least one of compounds having two or more carbon atoms and fluorine atom(s) such as  $C_2F_6$  and the like, or compounds of nitrogen atom(s) and fluorine atom(s) is contacted with a catalyst comprising at least one of alumina, titania, silica and zirconia at a temperature of about 400° to about 800°C in the presence of an effective amount of water vapor to convert F in the gas stream to HF.

[Advantages]

Fluorine compound-containing gas can be subjected to decomposition treatment with good efficiency.

[Selected Drawing]    Fig. 2